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GB 0965018 A EP 0131389 A1 US 4361654 A

(58) Field of search
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(54) Lead- and cadmium-free glass composition for glazing, enameling and decorating

(57) Lead- and cadmium-free glass compositions, consisting essentially of

0-12 % by wt. Li_2O
0-10 % by wt. MgO
3-18 % by wt. CaO
5-25 % by wt. B_2O_3
3-18 % by wt. Al_2O_3
3-18 % by wt. Na_2O
3-18 % by wt. K_2O
0-12 % by wt. BaO
25-55 % by wt. SiO_2
0-5 % by wt. TiO_2 and
0-<3 % by wt. ZrO_2

have an extraordinary combination of desirable properties for the glazing, enameling and decorating of glasses having low thermal expansion, such as borosilicate glasses as well as glass ceramics.

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LEAD- AND CADMIUM-FREE GLASS COMPOSITION FOR GLAZING, ENAMELING AND DECORATING, AND ITS USE

The invention relates to lead- and cadmium-free glass compositions for glazing, enameling and decorating, and their use for glasses having low thermal expansion, such as, in particular, borosilicate glasses, as well as glass ceramics.

The primary area of usage for such glasses or glass ceramics is constituted by laboratory appliances and cooking utensils resistant to temperature fluctuations, or especially also heatable plates, such as, for example, cooking surfaces.

Glazes are low-melting glasses utilized for protection, enhancement and/or alteration of the phsyical or chemical surface properties, for embedding, e.g. in electronics, or also simply for adornment and decoration of a great variety of glass articles, glass ceramic, ceramic, or porcelain.

Glazes usually consist of a transparent or translucent glass composition applied to the article in accordance with the conventional techniques, such as, for example, screen printing or brush application, in finely divided form, e.g. in the form of a paste. The finely ground glass powder is frequently also called frit.

Enamels are glazes containing coloring components, such as pigments; the pigment proportion in the enamel can amount to up to 30% by weight.

Pigments usually are oxides resistant with respect to the glaze, evoking the desired color impression in dependence on choice.

The glaze or the enamel is baked in at temperatures lying below the softening point of the article to be treated, the respective glass composition of the glaze and/or of the enamel being melted and forming a stable bond with the surface of the article.

Baking also serves for volatilization of the organic vehicles utilized as auxiliary agents for the application of the glaze or of the enamel.

In order to ensure an adequate and long-term adhesion of the glaze or enamel after baking and during subsequent practical usage, it is necessary in correspondence with previous theoretical considerations to carefully adapt, in particular, the thermal expansion coefficients of the article to be decorated and of the glaze or enamel to each other. In this connection, it has heretofore been considered desirable according to the state of the art for the glaze to exhibit a lower thermal expansion coefficient than the article to be glazed.

This was supposed to ensure that the glaze or the enamel, during cooling after baking, is exposed to tensile stress and accordingly does not exert on the properties of the support material any negative effects, especially strength-reducing effects.

Problems have been encountered heretofore in the glaze or enamel decoration of borosilicate glasses and, in particular, glass ceramics with low thermal expansion based on β-eucryptite or h-quartz mixed crystals produced by thermal treatment, the so-called ceraming of a suitable starting glass. Such glass ceramics are distinguished by a thermal expansion of $0 \pm 1 \times 10^{-6}/K$ in a temperature range of between 20° and 700° C.

Considering the thermal stability of these glass types, decorating with glaze or, respectively, enamel must take place at temperatures of below 1000° C.

In glass ceramics, the baking of the glaze or enamel is preferably conducted simultaneously with the ceramic-producing process, as a so-called direct baking step.

The glazes and enamels used heretofore for coating and/or decorating glasses of low thermal expansion coefficients and glass ceramics contain, in most instances, even today still lead and frequently even, in addition thereto, still cadmium.

The reason for the use of lead and cadmium in glazes is their positive effect on the melting properties, a marked lowering of the melt temperature with simultaneously optimum viscosity characteristic of the glaze or enamel, respectively.

In addition, these glases or enamels, after direct baking, exhibit adequate adhesive strength with respect to the carrier material and well satisfy the requirements posed under practical conditions, even over long usage periods.

This is the more surprising inasmuch as, in contrast to the theoretical demand for approximately the same thermal expansion coefficients between carrier material and glaze or enamel, these lead- and cadmium-containing glass compositions exhibit high thermal expansion coefficients of 5×10^{-6}/K up to even 10×10^{-6}/K.

The reason why these high-thermal-expansion glass compositions show adequate adhesion to substrates with practically no thermal expansion, such as, for example glass ceramic, is ascribed, insofar as this

phenomenon has been understood thus far, especially also to these additions of lead and possibly cadmium.

However, in the meantime, unfavorable toxicological effects of these substances on humans and the environment have resulted in a partial or entire prohibition of such lead or cadium compounds in decorative coatings.

A number of lead-free and cadmium-free products of this type have been proposed, therefore, in the literature.

Thus, it has been known from DE 3,405,708 C2 to provide a lead-free, cadium-free and zinc-free glass frit composition consisting of the components Al_2O_3, B_2O_3, SiO_2, Li_2O, ZrO_2, SnO_2 and of La_2O_3, CaO, SrO, BaO, Na_2O and F, and using same for a colored enamel to decorate articles of glass, glass ceramic and ceramic.

These glass frit compositions exhibit high contents of B_2O_3 and, in particular, also SnO_2 and/or La_2O_3.

Glass frit compositions with such high B_2O_3 contents with simultaneously low SiO_2 contents are hardly capable of satisfying high requirements with regard to chemical resistance, particularly acid resistance.

EP 0 267 154 Al relates to a lead- and cadmium-free glass frit composition consisting of Na_2O, ZnO, B_2O_3, SiO_2 and optionally of K_2O, Li_2O, CaO, SrO, BaO, Bi_2O_3, Al_2O_3, ZrO_2, TiO_2 and WO_3.

The glass frit composition contains 4.0 - 30.0 mol-% of ZnO. Also zinc compounds are considered to be toxic already in small concentrations, though less than those of cadmium, and therefore are not without problems, and thus undesirable, as a substitute for lead. Also, the chemical resistance of glasses having high ZnO contents is frequenty unsatisfactory in practical use.

WO 90/15782 discloses a lead-free glass composition with 30-51% by weight of SiO_2, 19-50% by weight of B_2O_3, 2-20% by weight of ZrO_2, up to 14% by weight of Na_2O, up to 6% by weight of K_2O, up to 19% by weight of ZnO, up to 5% by weight of Li_2O, and 2-8 parts of fluorine compounds per 100 parts of the other components of the composition. Here again, lead is primarily substituted by zinc.

EP 0 402 007 A1 relates to a glass composition with 30-70% by weight of SiO_2, 10-30% by weight of CaO, 0-20% by weight of ZnO, 3 -8% by weight of MoO_3, 0-20% by weight of B_2O_3, 0-25% by weight of Al_2O_3, 0-10% by weight of K_2O, 0-10% by weight of Na_2O, 0-10% by weight of MgO, 0-15% by weight of BaO, 0-7% by weight of Li_2O, 0-10% by weight of PbO, 0-5% by weight of SrO, 0-10% by weight of CeO, 0-0.1% by weight of CoO, and 0-5% by weight of P_2O_5.

Here, too, the composition contains possibly up to 20% of ZnO and, in addition, necessarily still at least 3% of MoO_3, the alkali resistance of which is inadequate due to the danger of the formation of molybdates. This composition furthermore will require a baking range of considerably above 1000° C.

U.S. Patent 4,970,178 claims a lead-free glass frit having the following components:
5.0-14.0 mol-% of Na_2O, 8.0-25.0 mol-% of ZnO, 6.0-13.0 mol-% of B_2O_3, 45.0-60.0 mol-% of SiO_2, 0-8.0 mol-% of K_2O, 0-5.0 mol-% of Li_2O , 0-8.0 mol-% of CaO, 0-8.0 mol-% of SrO, 0-9.0 mol-% of BaO, 0-10.0 mol-% of Bi_2O_3, 0-4.0 mol-% of Al_2O_3, 0-6.0 mol-% of ZrO_2, 0-7.0 mol-% of TiO_2, 0-1.0 mol-% of WO_3.

Also this glass frit necessarily contains ZnO.

EP 0 412 336 A1 discloses a pollutant-free orange-colored decorative paint made up of 15-30% by weight of an orange-colored pigment and 70-85% by weight of a glass frit wherein the frit consists of 35-60% by weight of SiO_2, 15-35% by weight of B_2O_3, 3-8% by weight of ZrO_2, 2-8% by weight of Al_2O_3, 10-18% by weight of Na_2O and/or K_2O and 2-6% by weight of Li_2O. This frit does not contain any CaO and is baked at 1000° C onto tiles.

The respective glass compositions according to the state of the art exhibit various, in part desirable, properties, but do not adequately meet high requirements.

Therefore, it is an object of this invention to indicate glass compositions free of lead, cadmium and other toxicologically objectionable components which satisfy high requirements, i.e. can be processed, in particular, without any problems in a broad and relatively low temperature range and, moreover, yield glazes and enamels, respectively, showing for use in industrial and domestic areas very good properties regarding adhesive strength, thermal stability, resistance to temperature fluctuations, abrasive resistance, and conspicuous abrasion, spotting tendency upon contamination, and chemical resistance to acids and alkalis.

According to the present invention, this object has been attained by a glass composition with

Li_2O	0	-	12	% by wt.
MgO	0	-	10	% by wt.
CaO	3	-	18	% by wt.
B_2O_3	5	-	25	% by wt.
Al_2O_3	3	-	18	% by wt.
Na_2O	3	-	18	% by wt.
K_2O	3	-	18	% by wt.
BaO	0	-	12	% by wt.
SiO_2	25	-	55	% by wt.
TiO_2	0	-	5	% by wt.
ZrO_2	0	-	<3	% by wt.

With glass compositions according to this invention, glazes and enamels can be produced which satisfy in excellent fashion the high requirements of practical use, without employing toxic or environmentally relevant materials.

It has been found surprisingly that these compositions according to the invention exhibit all of the desired properties even without additions of lead, cadmium, zinc, tin, and fluorine compounds.

It is supposed that the CaO proportion which lies markedly above the state of the art, in conjunction with the selection and usage quantities of the other components in accordance with this invention, leads to an intensive and positive interaction between the substrate glass and the glaze or enamel during the baking step, and thus to a stress-free and firmly adhering bond over an adequately long time period in practical use.

Superior adhesive strengths have been found with the glass compositions according to this invention in the thus-formed glazes after baking, following quenching tests and in continuous operation at 670° C. Even in case of relatively large layer thicknesses of the glaze, for example up to 9 μm, no spalling or peeling tendencies were displayed by the substrate glass, and this holds true even at extreme fluctuating temerature loads over longer periods of time. The thermal stability of the compositions is satisfactory and shows practically no change in color even after 75 hours at 670° C.

With good chemical resistance to acids and alkalis, the glaze compositions according to this invention have high gloss, low abrasion, and practically no conspicuous abrasion in grid-like and also solid application.

Glazes according to the composition of this invention can also be mixed any time without problems with pigments up to a proportion of 30% by weight and can then be used for the production of colored coatings and/or decorations. The pigments employed are customary oxide materials resistant to the glass compositions at the baking temperature.

However, the glaze can also be inherently colored, for example by the controlled addition of coloring oxides.

The composition of the glazing glass is first homogeneously melted and from the thus-formed glass, a glass powder having a grain size of < 10 μm, preferably 1 - 3 μm, is then produced by grinding, especially wet grinding. This powder is then made into a paste with a standard screen printing oil, e.g. on pine oil base, and applied according to generally known techniques, e.g. by screen printing, by transfer picture, or brush.

After baking on a glass of low thermal expansion or a glass ceramic, glaze layers are obtained with a thickness of between 2 and 9 μm. These layers, in spite of the very large differences in thermal expansion between the glaze or enamel and the substrate glass, show exellent adhesion and resistance to temperature fluctuations.

In a preferred embodiment, Li_2O on the order of magnitude of 4-10% by weight is added to the glass composition of this invention, and the CaO proportion is raised.

Both measures improve the melting ability of the glass composition to a marked extent, the increased CaO proportion entirely overcompensating for the slight impairment in chemical resistance incurred by the addition of Li_2O .

Other preferred embodiments contain, depending on the subsequent purpose of use, also additionally, for example, 8-10% by weight of BaO and/or, for instance, 6-10% by weight of MgO.

The addition of the facultative oxides proves advantageous, depending on the usage of the glass composition, where higher Li_2O contents generally entail a lowering of the baking temperature. BaO can serve as a replacement for CaO up to a certain proportion, but usually brings about an increase in baking temperature and thermal expansion.

Additions of TiO_2 improve acid resistance while ZrO_2 can further improve the resistance to alkalis.

The invention will be described in greater detail by the following examples.

Table I contains the compositions of Examples 1-17 of the glazes according to this invention in percent by weight, based on the oxide:

TABLE I

No.	1	2	3	4	5	6
Li_2O	10,0	4,0	10,0	4,0	4,0	4,0
B_2O_3	10,0	20,0	12,0	10,0	10,0	10,0
Na_2O	5,0	15,0	5,0	5,0	15,0	5,0
MgO	0,0	0,0	8,0	6,0	0,0	8,0
Al_2O_3	5,0	5,0	15,0	15,0	15,0	5,0
SiO_2	50,0	30,0	30,0	30,0	46,0	48,0
K_2O	5,0	15,0	5,0	15,0	5,0	15,0
CaO	5,0	11,0	15,0	5,0	5,0	5,0
BaO	10,0	0,0	0,0	10,0	0,0	0,0

No.	7	8	9	10	11	12
Li_2O	4,0	10,0	4,0	10,0	10,0	10,0
B_2O_3	10,0	20,0	20,0	20,0	20,0	10,0
Na_2O	15,0	15,0	5,0	5,0	5,0	5,0
MgO	8,0	8,0	0,0	0,0	8,0	0,0
Al_2O_3	5,0	7,0	5,0	15,0	5,0	15,0

SiO_2	30,0	30,0	46,0	30,0	32,0	30,0
K_2O	5,0	5,0	5,0	5,0	15,0	15,0
CaO	13,0	5,0	15,0	5,0	5,0	15,0
BaO	10,0	0,0	0,0	10,0	0,0	0,0

No.	13	14	15	16	17
Li_2O	4,0	10,0	10,0	9,4	6,4
B_2O_3	20,0	10,0	11,3	10,0	10,0
Na_2O	5,0	15,0	6,8	5,0	7,6
MgO	6,0	0,0	0,0	0,0	3,3
Al_2O_3	5,0	5,0	12,8	11,4	7,6
SiO_2	30,0	30,0	49,1	41,7	45,1
K_2O	5,0	15,0	5,0	5,0	5,0
CaO	15,0	5,0	5,0	15,0	5,0
BaO	10,0	10,0	0,0	2,5	10,0

Table II shows, for the compositions 1-17 of Table I, in each case the transition temperature (Tg) in ° C, the softening temperature (ST) in ° C, the processing temperature (PT) in ° C, as well as the thermal expansion coefficient (CTE) between 20° and 300° C in 10^{-6}/K.

T A B L E II

No.	Tg	ST	PT	CTE
1	454	567	690	10,18
2	374	469	596	14,49
3	433	533	840	11,41
4	382	495	830	12,38
5	444	557	750	11,50
6	447	568	756	10,98
7	374	490	700	13,62
8	365	447	597	13,65
9	511	610	765	9,20
10	422	513	639	10,83
11	378	456	630	13,13
12	385	515	755	12,60
13	466	567	689	10,51
14	300	400	430	16,40
15	435	537	780	11,02
16	432	531	750	11,48
17	436	543	705	11,14

Examples especially preferred according to this invention herein are compositions 1, 11, 15, 16, and 17, with transition temperatures in a range from 380° to 450° C, softening temperatures in a range from 460° to 570° C, processing temperatures from 630° to 780° C, and thermal expansion coefficients of 10.18 to 13.13 $\cdot$ 10^{-6}/K.

These compositions also display very good adhesive strengths, a high thermal and chemical resistance, and excellent usage properties during the course of the investigations performed according to the customary and conventional standard methods, as well as in long-term tests.

CLAIMS

1. A lead-and cadmium-free glass composition for glazing, enameling and/or decorating with up to 30% by weight of a pigment stable at the baking temperature, characterized in that the glass composition comprises the components

Li_2O	0	-	12	% by wt.
MgO	0	-	10	% by wt.
CaO	3	-	18	% by wt.
B_2O_3	5	-	25	% by wt.
Al_2O_3	3	-	18	% by wt.
Na_2O	3	-	18	% by wt.
K_2O	3	-	18	% by wt.
BaO	0	-	12	% by wt.
SiO_2	25	-	55	% by wt.
TiO_2	0	-	5	% by wt.
ZrO_2	0	-	<3	% by wt.

2. A glass composition according to claim 1, characterized in that it comprises the components

Li_2O	4	-	10	% by wt.
MgO	0	-	8	% by wt.
CaO	5	-	15	% by wt.
B_2O_3	10	-	20	% by wt.
Al_2O_3	5	-	15	% by wt.
Na_2O	5	-	15	% by wt.
K_2O	5	-	15	% by wt.
BaO	0	-	10	% by wt.
SiO_2	30	-	50	% by wt.
TiO_2	0	-	5	% by wt.
ZrO_2	0	-	<3	% by wt.

3. A glass composition according to claim 1, characterized in that it comprises the components

Li_2O	8	- 12	% by wt.
MgO	0	- 3	% by wt.
CaO	5	- 10	% by wt.
B_2O_3	5	- 13	% by wt.
Al_2O_3	5	- 10	% by wt.
Na_2O	5	- 10	% by wt.
K_2O	5	- 10	% by wt.
BaO	8	- 12	% by wt.
SiO_2	45	- 55	% by wt.
TiO_2	0	- 5	% by wt.
ZrO_2	0	- <3	% by wt.

4. A glass composition according to claim 1, characterized in that it comprises the components

Li_2O	8	- 12	% by wt.
MgO	6	- 10	% by wt.
CaO	5	- 10	% by wt.
B_2O_3	15	- 20	% by wt.
Al_2O_3	5	- 10	% by wt.
Na_2O	5	- 10	% by wt.
K_2O	10	- 15	% by wt.
BaO	0	- 5	% by wt.
SiO_2	30	- 40	% by wt.
TiO_2	0	- 5	% by wt.
ZrO_2	0	- <3	% by wt.

5. A glass composition according to claim 1, characterized in that it comprises the components

Li_2O	8	-	12	% by wt.
MgO	0	-	3	% by wt.
CaO	5	-	10	% by wt.
B_2O_3	5	-	13	% by wt.
Al_2O_3	10	-	15	% by wt.
Na_2O	5	-	10	% by wt.
K_2O	5	-	10	% by wt.
BaO	0	-	5	% by wt.
SiO_2	45	-	55	% by wt.
TiO_2	0	-	5	% by wt.
ZrO_2	0	-	<3	% by wt.

6. A glass composition according to claim 1, characterized in that it comprises the components

Li_2O	8	-	12	% by wt.
MgO	0	-	3	% by wt.
CaO	10	-	15	% by wt.
B_2O_3	5	-	13	% by wt.
Al_2O_3	10	-	15	% by wt.
Na_2O	5	-	10	% by wt.
K_2O	5	-	10	% by wt.
BaO	0	-	5	% by wt.
SiO_2	35	-	45	% by wt.
TiO_2	0	-	5	% by wt.
ZrO_2	0	-	<3	% by wt.

7. A glass composition according to claim 1, characterized in that it comprises the components

Li_2O	4	-	8	% by wt.
MgO	0	-	5	% by wt.
CaO	5	-	10	% by wt.
B_2O_3	5	-	13	% by wt.
Al_2O_3	5	-	10	% by wt.
Na_2O	5	-	10	% by wt.
K_2O	5	-	10	% by wt.
BaO	8	-	12	% by wt.
SiO_2	40	-	50	% by wt.
TiO_2	0	-	5	% by wt.
ZrO_2	0	-	<3	% by wt.

8. A glass composition according to claim 1, characterized in that it comprises the components

Li_2O	4	-	8	% by wt.
MgO	0	-	3	% by wt.
CaO	10	-	15	% by wt.
B_2O_3	15	-	20	% by wt.
Al_2O_3	5	-	10	% by wt.
Na_2O	5	-	10	% by wt.
K_2O	5	-	10	% by wt.
BaO	0	-	5	% by wt.
SiO_2	40	-	50	% by wt.
TiO_2	0	-	5	% by wt.
ZrO_2	0	-	<3	% by wt.

9. A glass composition according to any preceding claim, having a transition temperature of 300 - 510°C, a softening temperature of 400 - 610°C and a processing temperature of 430 - 840°C.

10. A glass composition according to claim 9, having a transition temperature of 380 - 450°C.

11. A glass composition according to claim 9 or 10, having a softening temperature of 450 - 570°C.

12. A glass composition according to claim 9, 10 or 11, having a processing temperature of 630 - 780°C.

13. A glass composition according to any preceding claim, characterized in that a glaze formed from the composition exhibits a thermal expansion coefficient of 9.20 to 16.40 x 10^{-6}/K.

14. A glass composition according to claim 13, wherein said glaze has a thermal expansion coefficient of 10.18 to 13.13 x 10^{-6}/K.

15. A glass composition according to claim 1, substantially as hereinbefore described in any one of Examples 1 - 17.

16. The use of a glass composition according to any preceding claim for the glazing, enameling and/or decorating of a glass having a thermal expansion of less than 5.0 x 10^{-6}/K.

17. A method decorating a glass having a thermal expansion of less than 5.0 x 10^{-6}/K, comprising baking a glass composition as claimed in any one of claims 1 to 15 onto said glass having a thermal expansion of less than 5.0 x 10^{-6}/K.

18. A method according to claim 17, wherein said glass is a borosilicate glass.

19. A method according to claim 17, wherein said glass is a glass ceramic.

20. A method according to claim 17, wherein said baking is effected whilst converting the glass to a glass ceramic.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

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GB 9300476.0

Relevant Technical fields

(i) UK Cl (Edition L) C1M (MAG)

(ii) Int Cl (Edition 5) C03C

Search Examiner

V V BAILEY-WOOD

Databases (see over)

(i) UK Patent Office

(ii)

Date of Search

17 MARCH 1993

Documents considered relevant following a search in respect of claims 1-20

Category (see over)	Identity of document and relevant passages		Relevant to claim(s)
X	GB 0965018	(JOHNS-MANVILLE) - see Examples 3 and 4	1
X	EP A1 0131389	(BURROUGHS CORP) - see Table on page 5	1
X	US 4361654	(NGK INSULATORS) - see Table 3(a)	1

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

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